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PROCESS FOR PREPARING VULCANIZED EPIHALOHYDRIN POLYMERS

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U.S. Cl. 260—45.8 N 8 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing vulcanized epihalohydrin polymers which comprises heating at least a polymer selected from the group consisting of a homopolymer of epihalohydrin and a copolymer of epihalohydrin with at least one other copolymerizable monomer in the presence of (A) 0.1–10 parts by weight of at least one compound selected from the group consisting of polyalkylenepolyamines, polyalkylenepolyamine carbamates and thioureas which are optionally substituted with alkyl groups of 1–4 carbon atoms leaving at least one hydrogen atom unsubstituted, (B) 1–20 parts by weight of magnesium oxide and (C) 0.2–5 parts by weight of 2-mercaptobenzimidazole.

This invention relates to a process for preparing vulcanized epihalohydrin homopolymers or copolymers with a novel system of vulcanizing agents.

Vulcanized epihalohydrin polymers have been prepared by conventional methods with such vulcanizing agents as polyamines (U.S. Pat. 3,026,270), an amine and at least one other agent selected from the group consisting of sulphur, dithiocarbamates, thiuram sulfides and thiazoles (U.S. Pat. 3,026,305), or 2-mercaptoimidazolines with compounds of Groups II or IV–A metals of periodic table (U.S. Pat. 3,341,491). Further, it is known that stabilized epihalohydrin polymer compositions are prepared with a polyamine cross-linking agent, a lead compound and a nitro-containing antioxidant (U.S. Pat. 3,239,486).

As a result of various studies on the heat-aging properties of vulcanized epihalohydrin polymers manufactured by the use of such vulcanizing agents and antioxidants, the inventors have found that a vulcanizate containing 2-mercaptoimidazoline, red lead and phenol- or amine-based antioxidants which are employed for ordinary diene rubber exhibits good heat-aging property. When a thiourea or an amine is employed in place of 2-mercaptoimidazoline and when magnesium oxide is used instead of red lead, the vulcanizate obtained shows obviously inferior heat-aging properties with an increased tendency toward softening and aging, which will be clarified by reference examples given below. However, applications of the vulcanizate are limited as the vulcanizate cannot be used for light-color blending because it contains red lead having staining qualities and also because it often takes on a metallic luster on its surface. Furthermore, since red lead tends to stain the mold, work required to remove such stains decreases the productivity.

The purposes of this invention, therefore, are to resolve all those problems and to produce vulcanized epihalohydrin polymers having excellent heat-aging properties.

The above purposes of this invention can be attained by the process which comprises heating a homopolymer of epihalohydrin or a copolymer of epihalohydrin with at least one other copolymerizable monomer in the presence of (A) at least one compound selected from the group consisting of polyalkylenepolyamines, polyalkylenepolyamine carbamates and thioureas which are optionally substituted with alkyl groups of 1–4 carbon atoms leaving at least one hydrogen atom unsubstituted, (B) magnesium oxide and (C) 2-mercaptobenzimidazole.

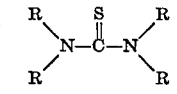
By the process of this invention, vulcanized epihalohydrin polymers with excellent heat-aging properties which are equivalent or superior to that which can be attained by the 2-mercaptoimidazoline/red lead vulcanizing system, and with limited staining properties enabling light-color blending, can be prepared.

A feature of this invention consists in the joint use of magnesium oxide and 2-mercaptobenzimidazole. Namely, whereas in the case of the conventional combination of vulcanizing agents and anti-oxidants, the heat-aging properties of a vulcanizate with magnesium oxide is inferior to that of vulcanizate with red lead. In the cases where polyalkylenepolyamines or their carbamates or thioureas and red lead or magnesium oxide and 2-mercaptobenzimidazole are employed jointly, the vulcanizate with magnesium oxide provides improved heat-aging properties. Although it is not yet clear what mechanism causes such a notable phenomenon, it is probably attributable to some multiplying effects caused by the coexistence of 2-mercaptobenzimidazole and magnesium oxide. Further studies by the inventors on the properties of 2-mercaptobenzimidazole have revealed that it has little antioxidizing properties unlike the amine- or phenol-based antioxidants in general use. For instance, it was found that its speed of oxygen absorption when uniformly dispersed in an epichlorohydrin polymer in a quantity of 2 percent by weight of said polymer, was 40 times that of phenyl-β-naphthylamine and 12 times that of styrenated phenol.

Furthermore, in this invention, magnesium oxide is employed as co-agent, and therefore the aforementioned various problems which are caused by the use of red lead can be completely avoided.

The epihalohydrin polymers vulcanizable in accordance with this invention comprise homopolymers of epichlorohydrin and/or epibromohydrin, copolymers of two different epihalohydrins, and copolymers of at least one epihalohydrin with at least one other copolymerizable monomer. Examples of other copolymerizable monomers include epoxides such as ethylene oxide, propylene, propylene oxide, butylene oxide, cyclohexene, oxide, butadiene monoxide, ethyl glycidyl ether, allyl glycidyl ether, tetrahydrofuran and trioxane; isocyanates such as ethyl isocyanate, phenyl isocyanate and 2,4-tolylene diisocyanate; alkyl acrylates such as ethyl acrylate and methyl methacrylate; cyclic acid anhydrides such as maleic anhydride, succinic anhydride and phthalic anhydride; vinyl ketones such as methyl vinyl ketone and cyclohexyl vinyl ketone; diolefins such as butadiene, isoprene and pentadiene; monoolefins such as ethylene, propylene and butene-1; nitriles such as acrylonitrile and methacrylonitrile; and styrene.

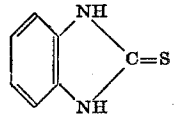
Of the agents used for vulcanizing those epihalohydrin polymers in this invention, diethylenetriamine, triethylenetetramine, hexamethylene-diamine, hexamethylenetetramine, piperazine (a cyclic polyalkylenepolyamine) and Trimene Base (trademark of Uniroyal, Inc.), hexamethylenediamine, carbamate and ethylene-diamine carbamate are representative examples of polyalkylenepolyamines and their carbamates of (A). Another example pertaining to (A) is thioureas with the following general formula:



wherein at least one of the R's is hydrogen, and the rest are alkyl groups of 1 to 4 carbons and whose representa-

tive examples are thiourea, mono-, di- or tri-ethyl thiourea and mono-, di- or tri-butyl thiourea.

2-mercaptobenzimidazole of (C) is an agent which is represented by the following formula:



After being blended in natural rubber, styrene butadiene rubber and acrylonitrile-butadiene rubber, it is generally utilized as a secondary antioxidant to prevent the breakage of rubber chains by peroxide decomposition or as a peptizer for natural rubber.

In the case of U.S. Pat. 3,026,305, for the vulcanization of an epihalohydrin polymer, 2-mercaptobenzothiazole which is employed together with amines and magnesium oxide acts as a vulcanization accelerator. In this invention, however, 2-mercaptobenzimidazole hardly exhibits a vulcanization accelerating function and acts as an agent to markedly improve the heat-aging property, and therefore, 2-mercaptobenzimidazole functions entirely differently in the respective cases. As clearly shown by the following examples, the heat-aging property can be drastically improved by the present invention.

In this invention, quantities of the three agents for each 100 parts by weight of epihalohydrin polymers are as follows: thioureas, polyalkylenepolyamines or polyalkylenepolyamine carbamates 0.1–10 (preferably 0.5–4) parts by weight, magnesium oxide 1–20 (preferably 3–10) parts by weight, and 2-mercaptobenzimidazole 0.2–5 (preferably 0.4–2) parts by weight.

The purpose of the present invention may be essentially attained by heating epihalohydrin polymers in the presence of the above-mentioned three components. Furthermore, by employing sulphur jointly, the tensile strength of the vulcanizates under normal conditions and after heat-aging may be even more improved. Volume of sulphur to be used is 0.1–5 (preferably 0.5–2) parts by weight against 100 parts of the polymer by weight.

Vulcanization in this invention may be attained by heating the polymer after being compounded with the aforementioned agents by ordinary methods such as roll mixing, Banbury mixing or solution mixing. Vulcanization temperature will be approximately 120 to 180° C. and vulcanization time 10 to 120 minutes. Furthermore, in order to minimize permanent set at high temperatures, it is sometimes heated at approximately 100 to 150° C. for about 1 hour to three days.

In addition to the aforementioned agents, other ordinary agents such as reinforcing agents, fillers, softening agents, plasticizers, stabilizers, activating agents and other anti-oxidants may be added as necessary.

This invention will be explained in greater detail by means of the following examples. Parts of components to be compounded in the examples will be shown by weight.

EXAMPLES 1–8

To various conventional vulcanizing agents and antioxidants, red lead or magnesium oxide was added as a co-agent, and comparison was made on the effects caused to heat-aging properties by each one of the above-mentioned coagents. After the components shown in Table 1 were kneaded together on 6-inch rolls at 30 to 40° C. and for approximately 30 minutes, the mixed compounds were vulcanized at 155° C. for 30 minutes. Then the heat-aging properties of the obtained vulcanizate (JIS K–6301, heating temperature: 150° C.) were measured. It is obvious from the results given in Table 1 that when the conventional vulcanizing agent and the antioxidant are combined, in each case, red lead is superior to magnesium oxide in improving the heat-aging property.

TABLE 1

	Example							
	1	2	3	4	5	6	7	8
Compounding components:								
Epichlorohydrin polymer [1]	100	100	100	100	100	100	100	100
Tin stearate	2	2	2	2	2	2	2	2
FEF carbon black	40	40	40	40	40	40	40	40
Phenyl-β-naphthylamine	1.5	1.4	1.5	1.5	1.5	1.5	1.5	1.0
Nickel dibutyl dithiocarbamate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
2-mercaptoimidazoline	2	2						
Dibutyl thiourea			3.8	3.8				
Trimene base					3	3		
Hexamethylenediamine carbamate [2]							1	1
Red lead	5		5		5		5	
Magnesium oxide		5		5		5		5
Heat-aging properties of the vulcanizates:								
Tensile strength (kg./cm.²) after—								
0 day [4]	142	113	148	121	139	119	151	125
3 days	166	81	47	31	112	60	86	10
6 days	153	62	7	S	14	S	S	S
9 days	132	53	[3] S		28			
Elongation (percent) after—								
0 day	480	550	660	710	420	440	430	430
3 days	290	460	340	680	280	620	370	740
6 days	260	430	250	S	310	S	S	S
9 days	260	410	S		190			
Hardness (JIS) after—								
0 day	65	69	65	61	75	74	71	75
3 days	77	68	67	56	80	68	78	68
6 days	74	66	54	S	73	S	68	S
9 days	74	66	51		88			

[1] Gechron 1000 made by The Japanese Geon Co. (hereinafter the same).
[2] Diak No. 1 made by Du Pont (hereinafter the same).
[3] "S" denotes that the vulcanizates softened and aged (hereinafter the same).
[4] No heat-aging (hereinafter the same).

EXAMPLES 9–18

A comparison was made as to the effects caused on heat-aging property when either magnesium oxide or red lead was added to hexamethylenediamine carbamate and 2-mercaptobenzimidazole. Furthermore, effects of volume change by 2-mercaptobenzimidazole were studied. Heat-aging properties (heating temperature: 160° C.) of vulcanizates which were obtained in the same manner as in Examples 1–8 are indicated in Table 2. Added for reference are the case of 2-mercaptoimidazoline/red lead as a representative known vulcanizing agent and the case where 2-mercaptobenzothiazole is employed in place of 2-mercaptobenzimidazole of this invention. As the results in Table 2 show, the heat-aging property of the vulcanizates can be improved by increasing the amount of 2-mercaptobenzimidazole in both systems. It is seen that at any level of consumption of 2-mercaptobenzimidazole, magnesium oxide system is superior and that the effects of using increased amount of 2-mercaptobenzimidazole are greater in this system. It is also seen that in comparison with the 2-mercaptoimidazoline/red lead system, magnesium oxide system presents, at 0.8 part or more by

weight, equal or improved heat-aging properties. It is obvious, furthermore, that when 2-mercaptobenzothiazole is used instead of 2-mercaptobenzimidazole required by this invention, resultant heat-aging properties are inferior to that attainable by this invention.

TABLE 2

	Example									
	9	10	11	12	13	14	15	16	17	18
Compounding components:										
Epichlorohydrin polymer	100	100	100	100	100	100	100	100	100	100
Tin stearate	2	2	2	2	2	2	2	2	2	2
FEF carbon black	40	40	40	40	40	40	40	40	40	40
Phenyl-β-naphthylamine	1	1	1	1	1	1	1	1	1	1
Nickel dibutyl dithiocarbamate	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Hexamethylenediamine carbamate	1	1	1	1	1	1	1	1	------	1
2-mercaptoimidazoline	------	------	------	------	------	------	------	------	1.5	------
Red lead	5	------	5	------	5	------	5	------	5	------
Magnesium oxide	------	5	------	5	------	5	------	5	------	5
2-mercaptobenzimidazole	0.4	0.4	0.8	0.8	1.2	1.2	2.0	2.0	------	------
2-mercaptobenzothiazole	------	------	------	------	------	------	------	------	------	2.0
Heat-aging properties of vulcanizates:										
Tensile strength (kg./cm.²) after—										
0 day	149	130	153	130	151	133	146	127	152	135
2 days	S	24	S	73	53	106	92	143	137	112
4 days	------	S	------	52	S	77	63	114	59	43
6 days	------	------	------	37	------	60	55	116	58	S
9 days	------	------	------	S	------	31	35	75	S	------
12 days	------	------	------	------	------	22	30	57	------	------
Elongation (percent) after —										
0 day	380	660	410	690	430	670	420	740	490	620
2 days	S	510	S	360	300	290	190	170	260	150
4 days	------	S	------	380	S	320	180	190	190	140
6 days	------	------	------	410	----	340	190	220	290	S
9 days	------	------	------	S	------	370	180	210	S	------
12 days	------	------	------	------	------	190	160	110	------	------
100% modulus (kg./cm.²) after—										
0 day	35	18	35	19	34	18	31	18	33	20
2 days	S	14	S	26	21	36	45	77	48	48
4 days	------	S	------	24	S	30	35	58	22	16
6 days	------	------	------	18	------	27	32	57	24	S
9 days	------	------	------	S	------	20	24	46	S	------
12 days	------	------	------	------	------	22	25	57	------	------
200% modulus (kg./cm.²) after—										
0 day	88	43	86	46	87	44	79	37	80	42
2 days	S	18	S	48	39	79	------	------	111	------
4 days	------	S	------	38	S	57	------	------	43	------
6 days	------	------	------	26	------	46	------	111	45	S
9 days	------	------	------	S	------	27	------	70	S	------
12 days	------	------	------	------	------	------	------	------	------	------
300% modulus (kg./cm,²) after —										
0 day	131	73	128	73	129	71	122	63	119	88
2 days	S	20	S	65	------	------	------	------	------	------
4 days	------	S	------	49	S	75	------	------	------	------
6 days	------	------	------	35	------	58	------	------	S	------
9 days	------	------	------	S	------	30	------	S	------	------
12 days	------	------	------	------	------	------	------	------	------	------
Hardness (JIS) after—.										
0 day	63	59	62	50	63	57	64	58	65	59
2 days	S	55	S	63	58	69	70	79	72	61
4 days	------	S	------	67	S	70	69	79	66	58
6 days	------	------	------	65	------	69	67	79	66	S
9 days	------	------	------	S	------	70	66	81	S	------
12 days	------	------	------	------	------	71	------	82	------	------

EXAMPLES 19–27

The heat-aging properties (heating temperatures: 150° C.) of vulcanizates made by employing various types of polyalkylene-polyamines in place of hexamethylenediamine carbamate which was used in Examples 9–16 and 18 were measured. The compounded components and the results of measurement are given in Table 3. It may be seen from Table 3 that with any amine, magnesium oxide system produces better heat-aging properties than red lead system and that through joint use of sulphur, even better tensile strength can be obtained even under a heated condition.

TABLE 3

	Example								
	19	20	21	22	23	24	25	26	27
Compounding components:									
Epichlorohydrin polymer	100	100	100	100	100	100	100	100	100
Tin stearate	2	2	2	2	2	2	2	2	2
FEF carbon black	40	40	40	40	40	40	40	40	40
Hexamethylenediamine	1.5	1.5	------	------	------	------	------	------	------
Triethylenetetramine	------	------	0.5	0.5	------	------	------	------	------
Diethylenetriamine	------	------	------	------	0.5	0.5	------	------	------
Trimene base	------	------	------	------	------	------	1.5	1.5	1.0
Red lead	5	------	5	------	5	------	5	------	------
Magnesium oxide	------	5	------	5	------	5	------	5	5
2-mercaptobenzimidazole	1	1	1	1	1	1	1	1	1
Sulphur	------	------	------	------	------	------	------	------	0.5
Heat-aging properties of the vulcanizates:									
Tensile strength (kg./cm.²) after—									
0 days	143	141	103	53	129	115	105	69	135
3 days	101	126	95	133	95	140	91	141	158
6 days	72	97	71	118	65	131	65	92	139
9 days	40	82	36	89	41	71	37	73	121
15 days	31	69	33	84	27	44	28	42	81
Elongation (percent) after—									
0 day	300	360	620	830	470	720	650	760	720
3 days	170	300	260	330	220	270	280	330	260
6 days	180	310	240	380	200	300	260	390	280
9 days	170	330	250	360	220	300	280	380	270
15 days	180	300	260	390	220	310	280	440	320
Hardness (JIS) after—									
0 day	75	71	65	58	65	61	66	63	67
3 days	78	82	72	75	70	78	70	79	81
6 days	70	81	65	76	64	79	65	75	80
9 days	68	83	63	75	61	79	61	76	82
15 days	65	85	58	73	57	74	58	77	78

EXAMPLES 28–33

The heat-aging properties (heating temperature: 160° C.) of vulcanizates made by using thioureas in place of hexamethylenediamine carbamate which was employed in Examples 9–16 and 18 as well as the effect of sulphur addition were measured in the same manner. The compounded components and the results of the measurement are shown in Table 4.

TABLE 4

	Example					
	28	29	30	31	32	33
Compounding components:						
Epichlorohydrin polymer	100	100	100	100	100	100
Tin stearate	2	2	2	2	2	2
FEF carbon black	40	40	40	40	40	40
2,2-methylene bis (4-methyl-6-tert-butylphenol)	2	2	2	2	2	2
Dibutyl thiourea	1	1	1	1		
Thiourea					1	1
Red lead	5		5		5	
Magnesium oxide		5		5		5
2-mercaptobenzimidazole	1	1	1	1	1	1
Sulphur			1	1	1	1
Heat-aging properties of the vulcanizates:						
Tensile strength (kg./cm.²) after—						
0 day	130	100	161	151	126	127
2 days	72	211	100	131	81	97
4 days	65	92	82	131	67	82
6 days	40	81	61	96	51	71
8 days	S	73	50	90	30	67
Elongation (percent) after—						
0 day	490	820	480	890	350	360
2 days	280	300	160	130	90	70
4 days	280	280	140	120	80	50
6 days	290	280	120	100	70	40
8 days	S	280	100	70	70	30
Hardness (JIS) after—						
0 day	58	56	61	59	72	71
2 days	62	68	72	76	76	82
4 days	60	70	72	80	76	84
6 days	56	71	65	82	74	88
8 days	S	70	60	84	72	90

EXAMPLES 34–37

In addition to the respective compounded components in Examples 10, 12, 14 and 16, sulphur was added in the quantity of one part by weight, and the heat-aging properties (heating temperature: 160° C.) of the vulcanizates obtained in the same manner were measured. The results are given in Table 5. The comparison between the results of Table 5 and the respective examples employing the different quantities of 2-mercaptobenzimidazole in Examples 10, 12, 14 and 16 shows that the heat-aging properties can be remarkably improved by sulphur addition.

TABLE 5

Example number	34	35	36	37
2-mercaptobenzimidazole, parts by weight	0.4	0.8	1.2	2.0
Heat-aging properties of the vulcanizates:				
Tensile strength (kg./cm.²) after—				
0 day	161	166	158	149
2 days	66	101	121	151
4 days	36	64	97	137
6 days	28	60	92	127
9 days	S	28	34	73
12 days		S	36	58
Elongation (percent) after—				
0 day	590	550	660	650
2 days	320	210	210	150
4 days	350	240	240	170
6 days	340	260	240	180
9 days	S	240	210	160
12 days		S	74	60
100% modulus (kg./cm.²) after—				
0 day	29	32	24	22
2 days	30	50	62	105
4 days	23	38	49	87
6 days	21	37	50	84
9 days	S	25	30	61
12 days		S		
200% modulus (kg./cm.²) after—				
0 day	63	71	52	49
2 days	51	96		
4 days	31	60	88	
6 days	26	55	85	
9 days	S	27	34	
12 days		S		
300% modulus (kg./cm.²) after—				
0 day	99	113	88	79
2 days	66			
4 days	35			
6 days	27			
9 days	S			
12 days		S		

What is claimed is:

1. A vulcanizable composition which comprises:

(a) 100 parts by weight of at least one polymer selected from the group consisting of:

(i) a homopolymer of an epihalohydrin, and

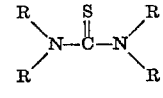
(ii) a copolymer of epihalohydrin and at least one monoepoxy monomer copolymerizable therewith;

(b) 0.1–10 parts by weight of at least one compound selected from the group consisting of:

(i) polyalkylenepolyamines,

(ii) alkylenediamine carbamates, and

(iii) thioureas with the following general formula



wherein each R can be hydrogen or an alkyl group of 1 to 4 carbon atoms and at least one R is hydrogen;

(c) 1–20 parts by weight of magnesium oxide; and

(d) 0.2–5 parts by weight of 2-mercaptobenzimidazole.

2. A vulcanizable composition according to claim 1 wherein the alkylenediamine carbamate is hexamethylenediamine carbamate.

3. A vulcanizable composition which comprises:

(a) 100 parts by weight of at least one polymer selected from the group consisting of:

(i) a homopolymer of an epihalohydrin, and

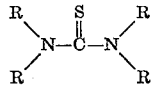
(ii) a copolymer of epihalohydrin and at least one monoepoxy monomer copolymerizable therewith;

(b) 0.1–10 parts by weight of at least one compound selected from the group consisting of:

(i) polyalkylenepolyamines,

(ii) alkylenediamine carbamates, and

(iii) thioureas with the following general formula



wherein each R can be hydrogen or an alkyl group of 1 to 4 carbon atoms and at least one R is hydrogen;

(c) 1–20 parts by weight of magnesium oxide;

(d) 0.2–5 parts by weight of 2-mercaptobenzimidazole; and

(e) 0.1–5 parts by weight of sulphur.

4. A vulcanizable composition according to claim **3** wherein the alkylenediamine carbamate is hexamethylenediamine carbamate.

5. A vulcanizate produced by a process which comprises heating the vulcanizable composition of claim **1.**

6. A vulcanizate produced by a process which comprises heating the vulcanizable composition of claim **2.**

7. A vulcanizate produced by a process which comprises heating the vulcanizable composition of claim **3.**

8. A vulcanizate produced by a process which comprises heating the vulcanizable composition of claim **4.**

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,790,524 Dated February 5, 1974

Inventor(s) Yoshiomi Saito et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 48 - change "2,4" to -- 2.4 --.

Column 4, Table 1, line 7 - change "1.4" to -- 1.5 --.

Column 4, Table 1, line 7 - change "1.0" to -- 1.5 --.

Column 5, Table 2, - in the Elongation (percent) after section on the 4 days line, change the second occurrence of "190" to -- 290 --.

Column 7, Table 4, line 8 - change "2,2-methylene" to -- 2,2'-methylene --.

Column 7, Table 4, line 18 - change "211" to -- 112 --.

Signed and sealed this 17th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents